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REMARKS

Page 9 of the subject specification has been amended to change the volume number of the cited reference from 28 to 23 to correct an obvious typographical error. Enclosed herewith is a copy of the article referred to in the specification. It is clear on the face of the article that the Journal of Polymer Science, Polymer Chemistry Edition, pages 429-444 in 1985 was volume 23 and not volume 28. No new matter is introduced by this correction.

Respectfully Submitted,

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Block Copolyurethanes Based on Polyoxytrimethylene Glycols

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Synopsis

Trimethylene oxide was polymerized to polyoxytrimethylene glycol by two synthetic routes. High molecular weight polytrimethylene oxide was synthesized using a coordination catalyst system consisting of triethylaluminum, acetylacetone, and water, then ozonized and reduced with lithium aluminum hydride in anhydrous ether to form hydroxyl end-capped polyoxytrimethylene glycol. In the second route, the polyoxytrimethylene glycols were synthesized directly by the cationic polymerization of trimethylene oxide with boron trifluoride/ethyl ether as catalyst and 1,4 butanediol as co-initiator. $(AB)_n$ block copolyether–urethane–ureas based on these polyoxytrimethylene glycols were synthesized and characterized by differential scanning calorimetry, and dynamic mechanical and stress–strain measurements.

INTRODUCTION

The polyether glycols used in the synthesis of most block copolyurethanes have traditionally contained an even number of carbon atoms in the chain repeat segment, i.e., polyoxyethylene glycol or polyoxytetramethylene glycol. Copolyurethanes prepared from these polyglycols show crystallization upon stretching because the chains can closely pack and thus induce crystallization. This limits their elasticity. Methyl groups have been introduced in the polyoxyethylene glycols to create an asymetric center (i.e., the polyoxypropylene glycols) to reduce this crystallization and improve elasticity. An alternate approach might be to synthesize copolyurethanes from the intermediate polyglycol, i.e., a polyoxytrimethylene glycol, which has an odd number of carbon atoms in the chain repeat unit, since the parent polyether, polytrimethylene oxide, has the lowest melting temperature of the three unsubstituted polyethers.[1]

This paper describes the preparation of several low molecular weight polyoxytrimethylene glycols and the properties of copolyether–urethane–ureas based on these polyglycols.

EXPERIMENTAL

Materials

Trimethylene oxide (Polysciences, Inc.) was purified by distillation over sodium hydroxide pellets at atmospheric pressure. (bp, 44.0–44.5°C at 640 mm Hg.)

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n-Heptane (Fisher Scientific) was dried over freshly cut sodium for 24 h, then distilled at atmospheric pressure through a spinning band column. (bp, 91°–92°C.)

Diethyl ether (Fisher Scientific) was distilled at atmospheric pressure. (bp, 30–31°C.)

1,4 Butanediol (Eastman Kodak) was distilled under reduced pressure [(bp, 94–95°C/2.0 mm Hg) and stored over molecular sieves (type 3A, Fisher Scientific).]

Acetylacetone (Matheson, Coleman and Bell) was distilled at atmospheric pressure. (bp, 128°C.)

Triethylaluminum was obtained as a 25 wt % solution in *n*-heptane (Ethyl Corporation) and was used as received.

Acetic anhydride and pyridine (Fisher Scientific) were used as received.

Dichloromethane (J. T. Baker) was dried over P_2O_5 for 24 h, then refluxed over P_2O_5 for 1 h, and finally distilled at atmospheric pressure through a spinning band column.

Methylene bis(4-phenyl isocyanate) (Multrathane M, Mobay) was distilled under reduced pressure. (bp, 141°C at 0.01 mm Hg.)

Ethylenediamine (J. T. Baker) was distilled under reduced pressure. (bp, 55°C at 60 mm Hg.)

4-Methyl-2-pentanone (J. T. Baker) was purified by distillation at atmospheric pressure. (bp, 110°C.)

N,N-Dimethylformamide (J. T. Baker) was distilled under reduced pressure. (bp 60°C at 27 mm Hg.)

Boron trifluoride etherate (Polysciences) was distilled under reduced pressure. (bp, 75–76°C at 62 mm Hg.)

Dimethyl sulfoxide (J. T.Baker) was distilled under reduced pressure. (bp, 68°C at 9.5 mm Hg.)

The 0.4*N* NaOH/CH_3OH was prepared by diluting the 0.4*N* NaOH analytical concentrate (0.4*N* NaOH DILUT-IT-Analytical Concentrate, J. T. Baker) with methanol in a 1000 mL volumetric flask.

Methyl sulfoxide-d_6 (99.5% D., Aldrich Chemical Co.) was used as received.

Chloroform-D (99.8% D., Stohler Isotope Chemicals) was used as received.

Synthesis of Polytrimethylene Oxide

Purified trimethylene oxide was polymerized using a coordination catalyst system[2] of triethylaluminum, acetylacetone and water in the molar ratio 1.0/1.0/0.5. To prepare the catalyst, 22.08 g (0.048 mol) of a 25 wt % solution of triethylaluminum in *n*-heptane was transferred by syringe to a 200 mL flamed flask containing a glass covered magnet. The transfer was done in a N_2 atmosphere glove box. Additional *n*-heptane (2.40 g) was then added. The flask was stoppered and cooled to 0°C for 1 h, then 10.68 g (0.146 mol) of diethyl ether and 4.80 g (0.048 mol) of acetylacetone were sequentially added dropwise with stirring. The solution was stirred for 1 h at 0°C, then 0.432 g (0.024 mol) of twice-distilled water was added over a 15-min period. The solution stirred for an additional hour at 0°C and then allowed to come to room temperature. The catalyst could be stored in a brown bottle at room temperature for up to 2 months before being used.

In a typical polymerization, a 200 mL polymerization tube was attached to a high-vacuum transfer line, then evacuated and flamed to remove moisture. *n*-Heptane was degassed and 90 mL transferred to the polymerization tube by externally cooling with liquid N_2. The tube was allowed to come to room temperature, flushed with N_2, then removed from the vacuum line and stoppered. 10.0 g (0.127 mol) of trimethylene oxide and 9.35 mL of the catalyst solution (containing 0.008 mol of triethylaluminum) was added under a N_2 flush and the polymerization tube reconnected to the high vacuum line and its contents solidified by cooling the tube externally with liquid N_2. The polymerization tube was then evacuated and sealed at the neck constricture. The polymerization tube was placed in a water bath and heated to 65°C for 19 h, then cooled to room temperature, the seal broken and 4.0 g (0.087 mol) of absolute ethanol added to stop the polymerization. The polymer adhered to the walls as a tough rubbery solid. This was removed, washed twice with 3% aqueous HCl solution, once with water, once with aqueous $NaHCO_3$ and four times with water (or until neutral). The polymer was cut into small pieces and dried under vacuum for 24 h. Inherent viscosity of the recovered polymer was 7.45 dL/g in benzene at 30°C (0.1% concentration).

Ozonation of Polytrimethylene Oxide

Polyoxytrimethylene glycols were obtained by ozonation of polytrimethylene oxide followed by reduction with $LiAlH_4$.[3] The molecular weight of the resultant polyglycol could be approximated from the following equation:

$$M(\text{g/mol of polyglycol}) = \frac{\text{wt of polytrimethylene oxide (mg)}}{\text{wt ozone (mg)}} \times 48(\text{gm/mol } O_3) \quad (1)$$

where M is the molecular weight of the polyglycol desired.

In a typical ozonation experiment, a Welsbach T-23 Ozonometer was set to deliver 95.3 mg of ozone p min. A 500 mL gas washing bottle containing 9.0 g of polytrimethylene oxide dissolved in 400 mL dried methylene chloride was connected to the ozonometer and the ozonized oxygen was bubbled through the solution for 66 min. The solution was then transferred to a 1000 mL flask and the solvent removed under vacuum on a rotary evaporator. The viscous polymer residue was dissolved in 100 mL of anhydrous ether and 1.10 g of lithium hydride ($LiAlH_4$) in 600 mL anhydrous ether slowly added. After 12 h, 30 mL of water was added to destroy the excess $LiAlH_4$. The ether layer was washed twice with 5% aqueous HCl, twice with water, once with 2% aqueous $NaHCO_3$ and four times (or until neutral) with water. The ether layer was dried over anhydrous $MgSO_4$ then the solvent removed on a rotary evaporator and the clear viscous polymer dried under vacuum. The various polyoxytrimethylene glycols prepared by this method are shown in Table I.

TABLE I
Molecular Weights of the Polyoxytrimethylene Glycol Samples Prepared by Ozonation of Polytrimethylene Oxide

Sample no.	Polytrimethylene oxide (g)	Ozone (mg)	Ozone absorbed (%)	Conversion (%)	$\bar{M}_n$ Calc.[a]	$\bar{M}_n$ Exp.[b]
1A	8.67	380	99.6	53.0	1100	1666
2A	27.0	1296	99.5	90.0	1000	1413
3A	27.0	1886	98.5	72.7	700	1252
4A	27.0	3240	99.8	60.4	400	1052

[a] Calculated from:[3]

$$M(\text{g/mol of polyglycol}) = \frac{\text{wt of polytrimethylene oxide (mg)}}{\text{wt ozone (mg)}} \times 48(\text{g/mol } O_3)$$

[b] By end-group analysis.

Synthesis of Polyoxytrimethylene Glycol

Purified trimethylene oxide was cationically polymerized to low molecular weight polyoxytrimethylene glycol using a boron trifluoride–ethyl ether catalyst system containing 1,4 butanediol as co-initiator.[4,5]

The catalyst system was prepared in a N_2 atmosphere glove box as follows: 3.375 g (0.0238 mol) of boron trifluoride–ethyl ether was transferred to a flamed 25 mL flask containing a glass covered magnet; 2.143 g (0.0238 mol) of 1,4 butanediol was added with stirring over a 5 min period; the mixture was then diluted with dry CH_2Cl_2 to form a 50% solution by volume. The flask was sealed with a rubber septum and stored at room temperature.

Under similar conditions, 4.06 g (0.07 mol) of trimethylene oxide and 36 ml of dry CH_2Cl_2 were added to a flamed 100 mL round bottomed flask (with a 10 cm long neck) containing a glass covered magnet. The flask was then sealed with a rubber septum and cooled to −45°C in a dry ice/acetone bath. 2.0 mL of the catalyst solution (containing 0.0047 mol each of boron trifluoride–ethyl ether and 1,4 butanediol) was then injected slowly into the vigorously stirred solution. The solution was stirred for 4 hours at −45°C, then 0.6 mL of a saturated solution of NaCl in water was injected to terminate the polymerization. The organic layer was separated and the solvent removed on a rotary evaporator. The resulting viscous residue was dissolved in 400 mL diethyl ether, then washed with 50 mL portions of 5% aqueous $NaHCO_3$ solution until the wash was basic to litmus, then with water until neutral to litmus. The ether solution was dried over anhydrous $MgSO_4$; excess ether was then removed using a rotary evaporator. The viscous polyoxytrimethylene glycol was dried under reduced pressure (0.01 mm Hg) for 4 h at room temperature, then stored over molecular sieves. Inherent viscosity of the polyether glycol was 0.09 in benzene at 30°C (0.5% concentration).

The various polyoxytrimethylene glycols prepared are shown in Table II. The number average molecular weights ($\bar{M}_n$) of polyoxytrimethylene glycols were determined experimentally by end-group analysis. In a typical deter-

Vol. 2
1985

TABLE II
Polyoxytrimethylene Glycol Samples Prepared with $BF_3 \cdot Et_2O$/Butanediol

Sample no.	Oxetane (mols)	Oxetane/Butanediol (mol ratio)	$BF_3 \cdot Et_2O$/Butanediol (mol ratio)	Concentration of Oxetane in CH_2Cl_2 (%)	Conversion (%)	Temperature (°C)	Time (h)	$\bar{M}_n$ Calc.	$\bar{M}_n$ Exp.[a]
1B	0.070	15	1[b]	10.0	79	−45	4.0	1832	1850
2B	0.066	15	2[b]	10.0	97	−45	4.0	1832	1811
3B	0.185	15	1[c]	25.0[d]	50	−50	4.0	1832	2740
4B	0.062	15	2[b]	10.0	94	−60	2.0	1832	3092
5B	0.155	15	1[b]	10.0	89	−65	3.0	1832	—
6B	0.138	15	2[b]	10.0	80	−65	3.0	1832	2063
7B	0.1722	8	1[b]	10.0	86	−60	4.0	1018	1944[e]
8B	0.1693	6	1[b]	10.0	85	−65	4.0	810	2486
9B	0.0492	6	0.5[c]	10.0	100	−20	2.0	764	780
10B	0.124	10	0.5[c]	10.0	42	−10	4.0	1050	1361
11B	0.1383	7.85	0.5[c]	10.0	81	−60	2.0	1000	1130

[a] Determined by end-group analysis.
[b] 50% (vol/vol) dilution of catalyst in CH_2Cl_2.
[c] No dilution of catalyst.
[d] Diethyl ether was used as the solvent.
[e] Loss of some catalyst due to loose syringe.

mination, approximately 1 g of the polyglycol was accurately weighed and transferred to a flamed, pressure bottle. 10.0 mL of a freshly prepared acetylating agent (10.6 mL acetic anhydride in 100 mL anhydrous pyridine) was pipetted into the bottle and the bottle immediately sealed with a crown cap containing a self-sealing gasket. The cap had two holes which allow liquids to be injected into the bottles through the self-sealing gaskets. All samples were run in duplicate. Two blanks, containing the acetylating agent alone, were also run. The samples and blanks were heated at 106°C in a vapor bath for 75 min. The bottles were cooled to room temperature and 10 mL of pyridine and 10 mL of water were injected into each of the bottles through the gasket. The bottles were heated for another 10 min, then cooled to room temperature and their contents poured into separate 250 mL Erlenmeyer flasks. The bottles were rinsed with 25 mL methanol and 40.0 mL of 0.4 N $NaOH/CH_3OH$ was pipetted into each flask. Six drops of 1% phenolphthalein in pyridine were added to each flask and titrated against 0.4*N* $NaOH/CH_3OH$ to a pale pink color persisting for at least 15 s. The $\overline{M}_n$ of the polyglycol was calculated as follows[6]

$$\overline{M}_n = \frac{Y \times 1000 \times \text{wt(g) polyglycol}}{N \times (B - S)}$$

where Y = number of OH groups per polymer chain; N = normality of $NaOH/CH_3OH$; B = titer of blank, in mL; and S = titer of sample in mL.

Synthesis of Copolyether-Urethane-Ureas

In a typical preparation 6.71 g (0.048 mol) of polyoxytrimethylene glycol ($\overline{M}_n$ 1413) was transferred to a flamed 250 mL three-necked flask fitted with a thermometer, gas inlet, condenser protected with a drying tube and magnetic stirrer. 12.5 mL of 4-methyl 2-pentanone, 2.39 g (0.096 mol) of methylene bis(4-phenyl isocyanate) and 12.5 ml dimethyl sulfoxide were added under a N_2 flush. The solution was heated at 85°C for 1.5 h with stirring, then 0.186 g (0.048 mol) of ethylenediamine in 30 mL dimethyl sulfoxide was added. After 30 min, the viscous solution was poured into deionized water to precipitate the polymer. The polymer was washed several times with water, then cut into small pieces and dried under a vacuum at room temperature for 24 h. Inherent viscosity of the final product was 0.42 dL/g in *N,N*-dimethylformamide at 30°C (0.5% concentration). The copolymers prepared are tabulated in Table III.

Films of the copolyurethanes were obtained by casting a 10% *N,N*-dimethylformamide solution of the polymer onto glass plates. The castings were dried at 65°C in a forced draft oven for 45 min, then dried under vacuum for 24 h at room temperature.

Characterization of Copolymers

Infrared spectra of the polymers were obtained with a Perkin-Elmer 521 Grating Spectrometer.

Proton nuclear magnetic resonance (^{1}H-NMR) and ^{13}carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a JEOL FX-270 NMR

TABLE III
Properties of Copolyether–Urethane–Ureas Prepared from Polyoxytrimethylene Glycols

Polymer no.	Polyglycol $\bar{M}_n$	Polyglycol Sample no.	η_{inh}[a]	PMT[b] (°C)
1C	1413	2A	0.42	180
2C	1252	3A	0.40	181
3C	780	9B	0.48	> 226(deg.)
4C	1130	11B	0.39	187
5C	1361	10B	0.39	184
6C	1944	7B	0.38	194
7C	2063	6B	0.52	181
8C	2486	8B	0.43	178

[a] Inherent viscosities were determined in *N,N*-dimethylformamide at 30°C and 0.5% concentration.
[b] Polymer melting temperature.

Spectrometer operating at 270 mHz and 67.8 mHz, respectively, in Fourier Transform mode at ambient temperature. Deuterochloroform ($CDCl_3$) and deuterodimethyl sulfoxide (DMSO-d_6) were used as solvents to form the polymer solutions of concentration 2–5% for ^{1}H-NMR and 10–15% for ^{13}C-NMR spectra, respectively. Chemical shifts were calculated based on 7.26 ppm for $CDCl_3$ and 2.5 ppm for DMSO-d_6 from TMS in ^{1}H-NMR and 77.17 ppm for $CDCl_3$ from TMS (middle peak of the $CDCl_3$ triplet) in ^{13}C-NMR spectra, respectively.

Tensile properties of copolymers were measured on an Instron Tensile Tester (Table Model 113A). The measurements were made using 1.3 cm × 0.4 cm dog bone samples at room temperature. Crosshead speed was 50.8 mm/min.

Dynamic mechanical measurements were made with a direct reading dynamic viscoelastometer (Rheovibron DDV-II-C), at frequencies of 110, 11, and 3.5 Hz in the temperature range of −170°C–150°C. The heating rate was approximately 1°C/min and the samples dimensions were 3.0 cm × 0.4 cm × .01 cm. A dry nitrogen purge was used to avoid the absorption of moisture by the sample.

Thermal analysis of the copolymers was made using a differential scanning calorimeter (Perkin Elmer DSC II). Sample size ranged from 2–8 mg with an accuracy of ±0.02 mg.

RESULTS AND DISCUSSIONS

Polytrimethylene Oxides and Polyoxytrimethylene Glycols

The polymerization of trimethylene oxide with a triethylaluminum/acetylacetone/water coordination catalyst system[2] gave good yields of high molecular weight polymer when a 21:1 molar ratio of trimethylene oxide to triethylaluminum was used. Based on intrinsic viscosity measurements which ranged from 5.37 to 7.45 in benzene at 30°C, molecular weights were calculated to be 4.24×10^5 to 6.45×10^5 using the Mark–Houwink relationship with $K = 21.9 \times 10^{-3}$ mL/g and $\alpha = 0.78$.[7] Ozonation of these polytrimethylene oxides followed by reduction[3] gave a series of polyoxytri-

methylene glycols shown in Table I. It was of interest to note that the molecular weights, determined by end group analysis were always higher than the theoretical molecular weights calculated on the basis of the amount of ozone absorbed by the polymer. This could be due to the prolonged time of ozonation resulting in the loss of polymer thereby giving a higher molecular weight than expected.

As an alternate approach to polyoxytrimethylglycols which might also result in a narrower molecular weight distribution, trimethylene oxide was cationically polymerized directly to the polyoxytrimethylene glycols using BF_3–etherate 1,4-butanediol as the co-initiator.[4,5] This approach appeared to give fairly good control of the polyglycol molecular weight (see Table II). The molecular weight of the polyglycols is dependent on the monomer to butanediol mole ratio rather than the monomer to BF_3:Et_2O mole ratio.

The incorporation of butanediol into the polymer chain has been confirmed by ^{1}H-NMR and ^{13}C-NMR spectra. By comparing the ^{1}H-NMR of polyoxytrimethylene glycol prepared by ozonation (Sample 2A) to that prepared by cationic polymerization (Sample 1B), (see Figures 1 and 2, respectively), a small peak at 1.52 ppm in Figure 2 is absent in Figure 1. Based on calculations,[8,9] this peak was assigned to the methylene protons (C—$\underline{CH_2}$—$\underline{CH_2}$—C), of the 1,4-butanediol incorporated into the polymer chain during the cationic polymerization of trimethylene oxide.

The sharp peak at 1.73 ppm was assigned to the methylene protons, C—$\underline{CH_2}$—C, of the trimethylene oxide repeat unit while the largest peak at 3.39 ppm was assigned to the methylene protons, O—$\underline{CH_2}$—C, of the trimethylene oxide repeat unit. Protons on the carbon adjacent to the end groups appear as small peaks at 3.50 and 3.60 ppm.

The ^{13}C-NMR spectra of these same samples are shown in Figures 3 and 4, respectively. The three additional peaks appearing at 26.50, 62.26, and 70.60 ppm in the spectra in Figure 4 and found to be absent in the spectra in Figure 3, are assigned, based on calculation,[8] to the carbon atoms from the butanediol molecule incorporated into the trimethylene oxide polymer chain. The peak at 62.26 ppm appears to be the terminal carbon of butanediol which carries the —OH group. The cluster of three small peaks at 77 ppm are due to the solvent $CDCl_3$. By calculation[8] the doublet at 29.99

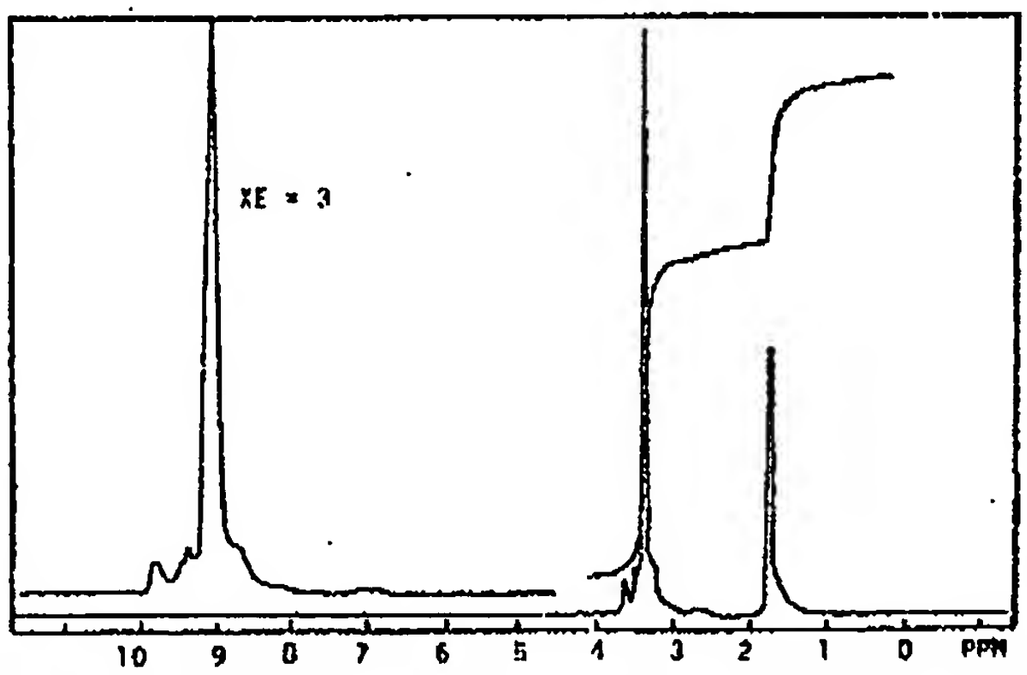

Fig. 1. ^{1}H-NMR spectrum of polyoxytrimethylene glycol (sample 2A, mol wt. 1413) in $CDCl_3$.

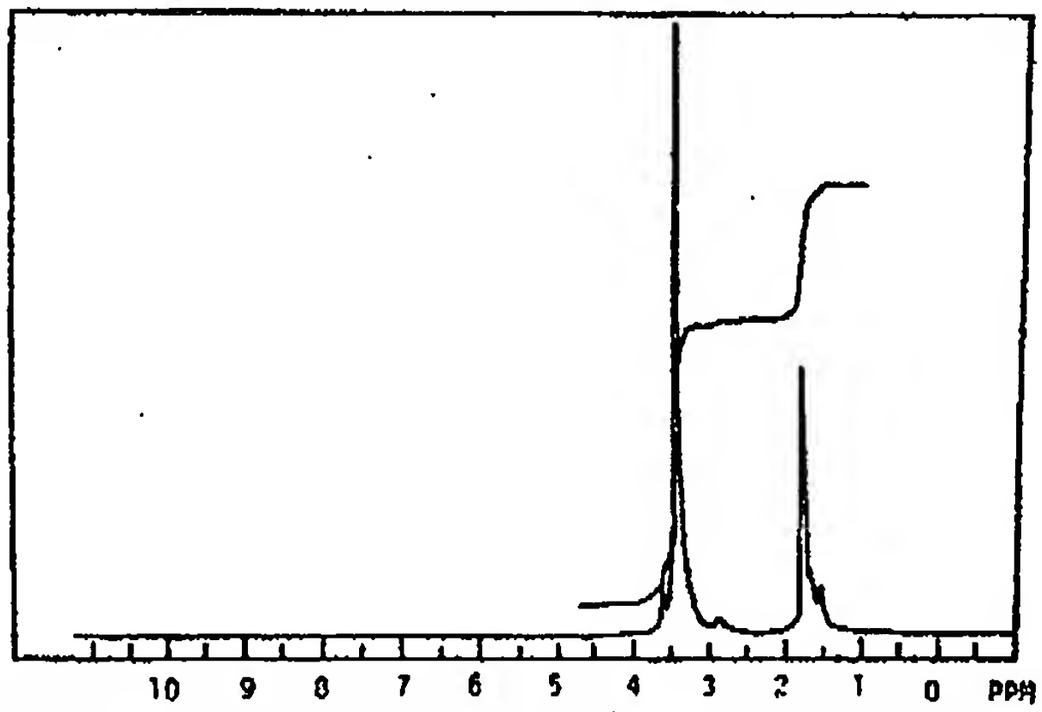

Fig. 2. ^{1}H-NMR spectrum of polyoxytrimethylene glycol (sample 11B, mol. wt. 1130) in $CDCl_3$.

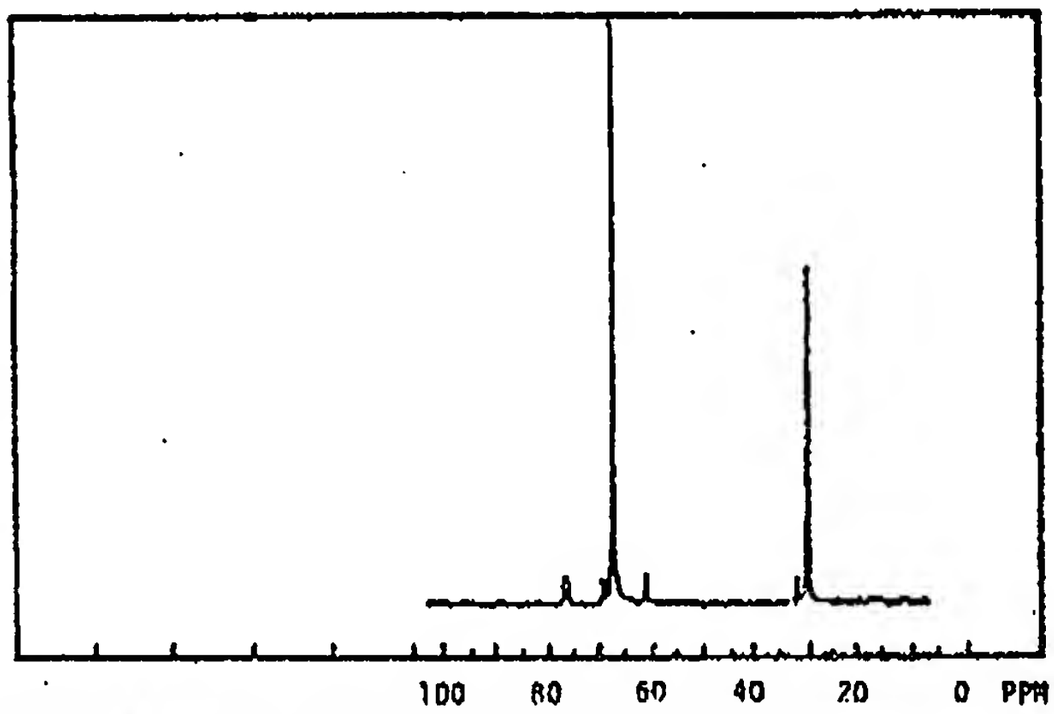

Fig. 3. ^{13}C-NMR spectrum of polyoxytrimethylene glycol (Sample 2A, mol. wt. 1413) in $CDCl_3$.

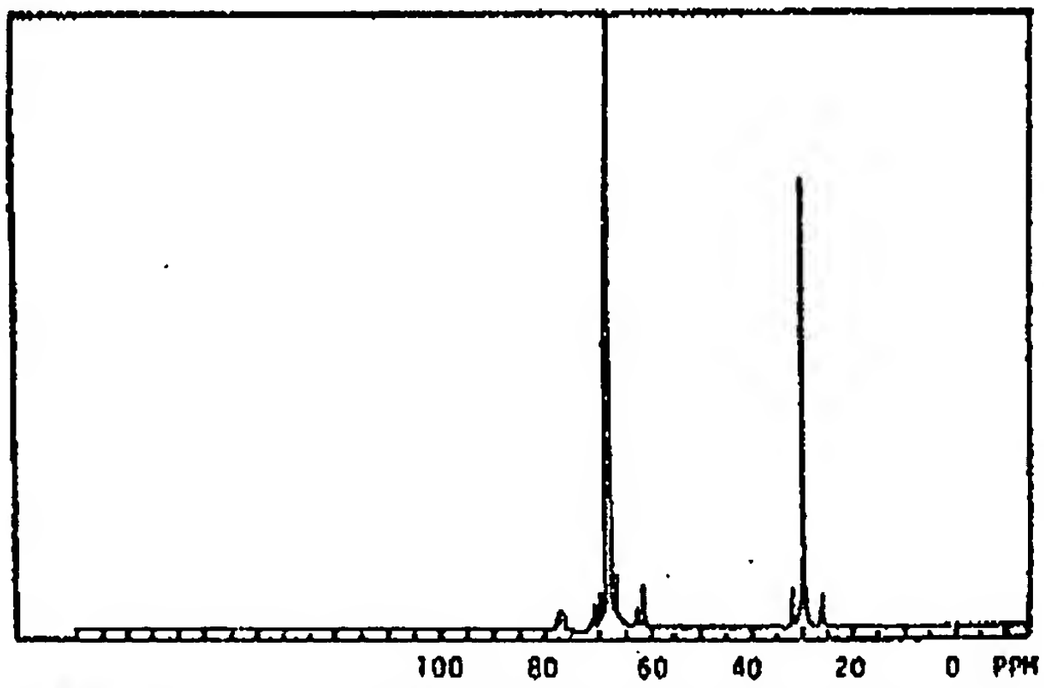

Fig. 4. ^{13}C-NMR spectrum of polyoxytrimethylene glycol (Sample 11B, mol. wt. 11B) in $CDCl_3$.

ppm is assigned to the C—$\underline{CH_2}$—C carbon, the small peak at 61.10 ppm is due to the terminal carbon which carries the —OH group, and the biggest peak at 67.70 ppm is assigned to the O—$\underline{CH_2}$ carbons of the trimethylene oxide repeat unit.

The polyoxytrimethylene glycols were readily polymerized to copolyether–urethane–ureas using a modified two-step solution polymerization.[10] The copolymers synthesized are tabulated in Table III. As expected, the polymer melt temperature of the copolymers decreased with an increase in the molecular weight of the polyether segments. However, polymer 6C shows an anomalous melt temperature (194°C) which could not be explained.

The block copolyoxytrimethylene ether–urethane–ureas would be expected to separate into domain matrix structures.[11,12] This is supported by dynamic mechanical measurements. See Figure 5 for the storage modulus, E' versus temperature curves for the copolymers based on polyoxytrimethylene glycols of molecular weights 780, 1251, and 1413. It would appear, however, that the separation is not as complete (i.e., there is some phase mixing) when the polyether glycol molecular weight is below 1200. This is not unexpected and has been seen in other copolymer systems.[13] It is noteworthy that at molecular weights greater than 2000, the E′ versus temperature curves for the copolymers show an additional transition, possibly indicating a three phase system. The tan δ vs. temperature curves (at 11 Hz) for these same samples (see Figure 6) show three distinct loss peaks. The γ-loss peak, assigned to a local motion of the methylene segments in

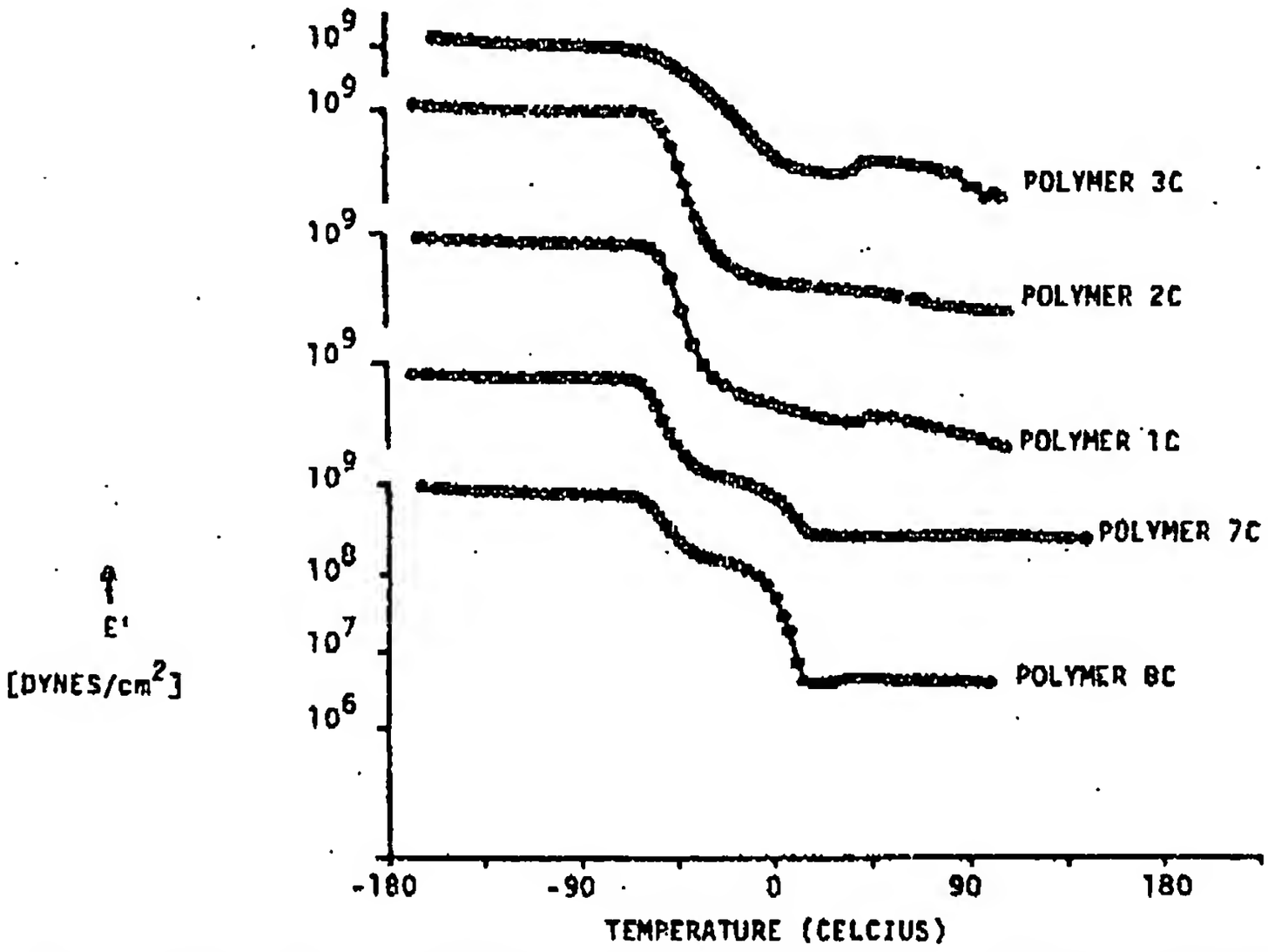

Fig. 5. Storage modulus, E' versus temperature curves for several copolyoxytrimethylene ether–urethane–ureas. Polyglycol mol. wts. were: 1C, 1413; 2C, 1252; 3C, 780; 7C, 2063; and 8C, 2486.

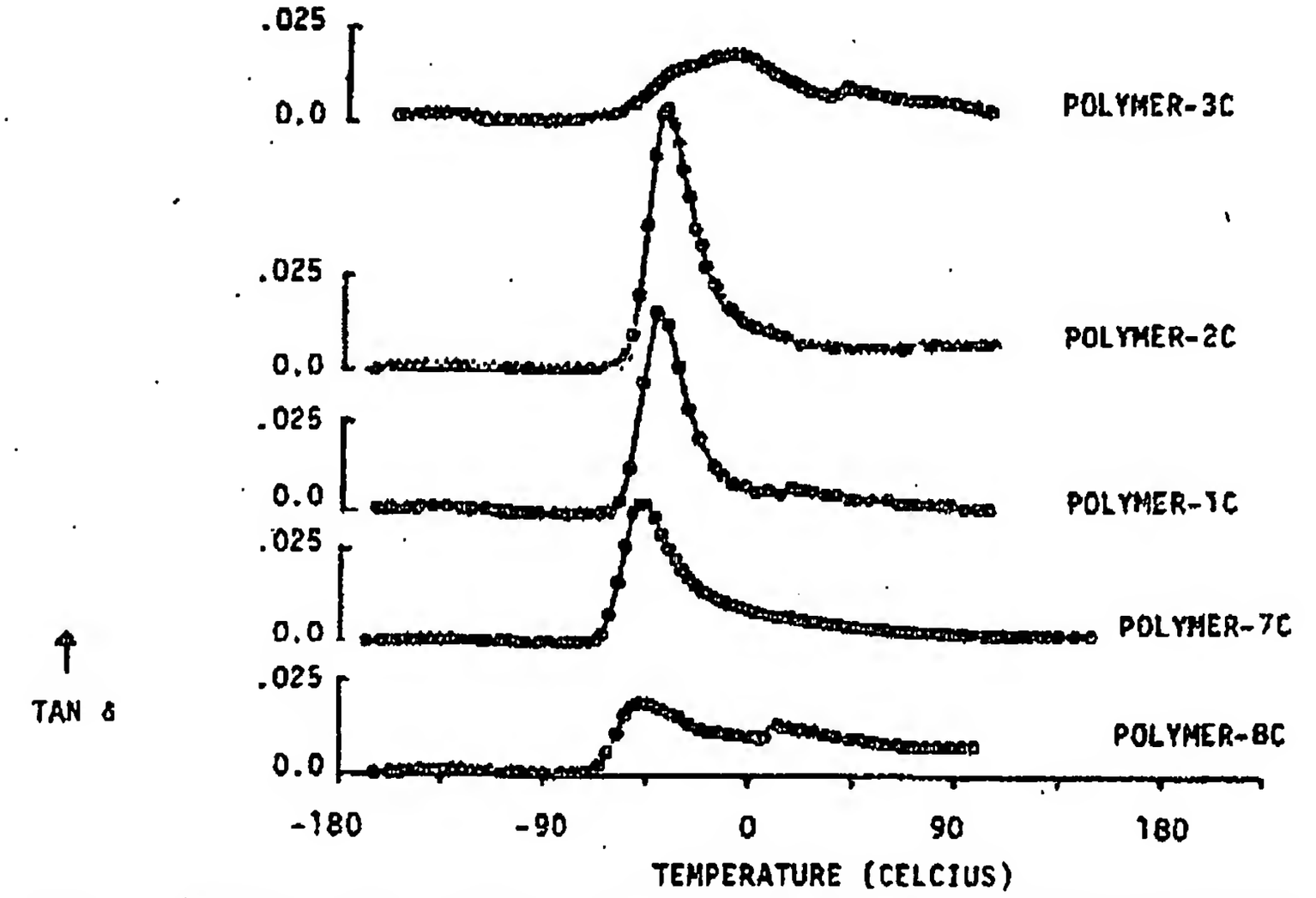

Fig. 6. Loss factor, tan δ versus Temperature curves for several copolyoxytrimethylene ether-urethane-ureas at 11 Hz. Polyglycol mol. wts. were: 1C, 1413; 2C, 1252; 3C, 780; 7C, 2063; and 8C, 2486.

the chain backbone of the polyether segments in the copolymers, was found to vary from −136.5°C to −129.4°C as the molecular weight of the polyether segments in the copolymers increase from 780 to 2486. The β-loss peak is associated with the glass transition temperature (T_g) of the polyether segments in the copolymers and varies from −46°C to −40°C as the molecular weight of the polyether segments decreases from 2480 to 1251, then abruptly increases to −8.5°C as the molecular weight further decreases to 780. This abrupt increase in T_g with decreasing polyether segment length and the presence of the α′ peak at 39.5°C has been proposed[13] to result from reduction in the overall freedom of motion of short polyether segments due to the constraining effects of the domains.

For the copolymers with polyether molecular weights from 1251 to 2486, an α-loss peak is observed. Similar relaxations have again been observed in other copolyurethanes with long ether segments.[13] In the case of copolyurethanes based on polyoxytetramethylene glycol, this relaxation was assigned to the crystalline portion of the polyether segments.[14] The variation of the loss peaks with the molecular weight of the polyether segments of these block copolymers are tabulated in Table IV.

The apparent activation energy of transition ($\Delta H^{\ddagger}$) of the β-relaxation process for these copolymers was calculated (see Table IV). This normally would show a decrease in $\Delta H^{\ddagger}$ with increasing molecular weight of the polyether segments of copolymers since longer chains should have more freedom of motion than shorter chains at T_g. In general, this is seen. There is a drop in $\Delta H^{\ddagger}$ from 91 Kcals for the 780 molecular weight segment to ca. 50 Kcal for the 1251 and 1413 molecular weight segments. There is a

TABLE IV
Loss Peak Maxima and $\Delta H^{\ddagger}$ of Block Copolyurethanes from Dynamic Mechanical Measurements

Polymer no.	$\overline{M}_n$ Polyglycol	γ^a (°C)	β^b (°C)	α^b (°C)	$\Delta H^{\ddagger c}$ (KCal)
3C	780	−136.5	−8.5	39.5[d]	91
2C	1252	−132.0	−40.0	18.0	48
1C	1413	−134.0	−40.0	17.0	50
7C	2063	−129.4	−46.0	11.0	46
8C	2486	−129.4	−46.0	13.0	41

[a] From plots of E' vs. T(°C).
[b] From plots of E'' vs. T(°C).
[c] $\Delta H^{\ddagger}$ can be calculated from the equation[18]

$$\Delta H^{\ddagger} = \frac{-R\partial \ln \omega}{\partial(1/T_{max})}$$

where R = the gas constant (1.987 cal/mol/K), ω = the frequency of measurement, in Hz; T_{max} = the transition temperature, in °K; and $\Delta H^{\ddagger}$ = the apparent activation energy of transition.
[d] This is considered an α' loss peak.

further drop, though only slight, for the 2063 and 2486 molecular weight segments. This leveling off of $\Delta H^{\ddagger}$ may indeed indicate some restrictions to the motion of the longer polyether segments, possibly due to crystallization of these segments.

These same copolymers, plus a polyoxytrimethylene glycol and a polytrimethylene oxide (molecular weight > 100,000), were analyzed by Differential Scanning Calorimetry (DSC). The thermograms are shown in Figure 7 and the data tabulated in Table V. While the thermograms for copolymers

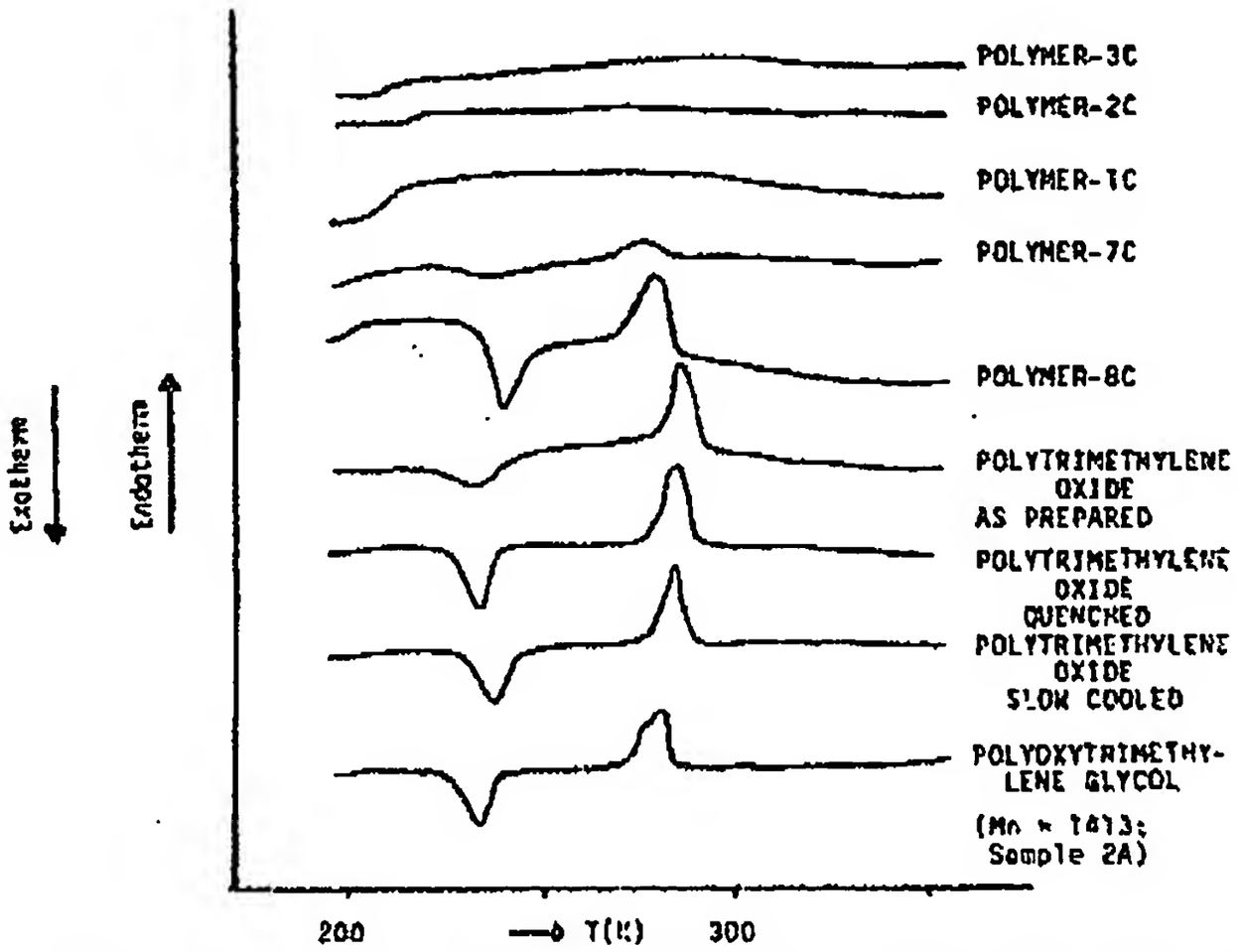

Fig. 7. Differential scanning calorimetry curves for several copolyoxytrimethylene ether-urethane-ureas, polyoxytrimethylene glycol, and polyoxetane. Polyglycol mol. wts. were: 1C, 1413; 2C, 1252; 3C, 780; 7C, 2063; and 8C, 2486.

Vol. 23
1985

TABLE V
Crystallization (T_c) and Crystallization Melting (T_m) Temperatures of Block Copolyurethanes, Polytrimethylene Oxide and Polyoxytrimethylene Glycol from DSC Measurements

Polymer no.	$\bar{M}_n$ polyglycol	Thermal treatment	T_c (°C)	T_m (°C)
3C	780	None	None	None
2C	1251	None	None	None
1C	1413	None	None	None
7C	2063	None	−40.5	2.5
8C	2486	None	−34.5	5.5
Polytrimethylene oxide	>100,000	None	−43.2	14.3
Polytrimethylene oxide	>100,000	Quenched[a]	−42.5	14.5
Polytrimethylene oxide	>100,000	Slow cooled[b]	−36.0	10.0
Polyoxytrimethylene glycol, 2A	1413	Slow cooled[b]	−35.0	9.0

[a] Quenched from 127−−73°C at 320°/min rate.
[b] Slow cooled from 127−−73°C at 10°/min rate.

7C and 8C (where the molecular weight of the polyether segment is >2000) exhibit an endothermic and an exothermic peak for each sample; those for samples 1C, 2C and 3C (molecular weight of polyether segment <1500) exhibit no similar peaks. To understand this behavior, a high molecular weight polytrimethylene oxide homopolymer was also studied by DSC. The thermograms of polytrimethylene oxide (with and without thermal treatment), also show endothermic and exothermic peaks similar to thermograms of copolymers 7C and 8C. These peaks shown by polytrimethylene oxide are indicative of crystallization and subsequent melting of crystals.[15] Although both samples supercooled, the slowly cooled polytrimethylene oxide (from 127°C to −73°C at the rate of 10°/minute) crystallized at a higher temperature than the sample quenched from 127°C to −73°C in liquid N_2. The thermogram of the polytrimethylene oxide as prepared (Fig. 7), while showing a smaller crystallization peak, does indicate the presence of crystallization in this material. It has been shown that there are three crystalline modifications present in polytrimethylene oxide and their crystal structures have already been established by X-ray studies.[15] Hence, the presence of crystallinity in the longer polyether segments of the copolymer is not unexpected; for shorter polyether segments the crystallization in the copolymers is inhibited by the presence of the domains.

A typical IR spectra of the copolyether–urethane–ureas is shown in Figure 8. The sharpness of the NH band at 3295 cm^{-1} indicates complete hydrogen bonding (as there is no free N—H peak at 3450 cm^{-1}). However, the splitting of both the urethane carbonyl at 1740 cm^{-1} and the urea carbonyl at 1690 and 1655 cm^{-1} indicates some free (i.e., nonhydrogen bonding) carbonyls which would result from some —NH hydrogen bonding to ether oxygens. This supports the dynamic mechanical data which indicates incomplete phase separation.

The elasticity of the copolyether–urethane–ureas is mainly dependent upon the chemical structure and the molecular weight of the polyether soft